

chain nodes :

7 14 16 21 22 24 25

ring nodes :

1 2 3 4 5 6 8 9 10 11 12 13

chain bonds :

4-7 11-16

ring bonds :

1-2 1-6 2-3 3-4 4-5 5-6 8-9 8-13 9-10 10-11 11-12 12-13

exact/norm bonds :

4-7 11-16

normalized bonds :

1-2 1-6 2-3 3-4 4-5 5-6 8-9 8-13 9-10 10-11 11-12 12-13

G1:CH3,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu,MeO,EtO,n-PrO,i-PrO,n-BuO,i-BuO,s-BuO,t-BuO,PhO,H

Match level :

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:CLASS8:Atom 9:Atom 10:Atom 11:Atom 12:Atom
13:Atom 14:CLASS15:Atom 16:CLASS21:CLASS22:CLASS24:CLASS25:CLASS26:Atom 27:Atom
28:Atom 29:Atom

fragments assigned product role:

containing 1

fragments assigned reactant/reagent role:

CAS ONLINE PRINTOUT

=> d his

(FILE 'HOME' ENTERED AT 09:11:47 ON 21 SEP 2006)

FILE 'REGISTRY' ENTERED AT 09:11:57 ON 21 SEP 2006

L1 0 S US20060052632/PN

FILE 'CAPLUS' ENTERED AT 09:12:34 ON 21 SEP 2006

L2 1 S US20060052632/PN
 L3 3798 S DEHYDRATION REACTION/IT
 L4 6152 S PHENOLS, REACTIONS/IT
 L5 1 S AKALI METAL/IT
 L6 0 S L3 AND L4 AND L5
 L7 86862 S ALKALI METAL/IT
 L8 1 S L7 AND L4 AND L3
 L9 12 S L4 AND L3

FILE 'HOME' ENTERED AT 09:17:38 ON 21 SEP 2006

FILE 'REGISTRY' ENTERED AT 09:21:45 ON 21 SEP 2006

FILE 'CAPLUS' ENTERED AT 09:21:49 ON 21 SEP 2006

L10 47272 S ALKALINE/IT
 L11 0 S L4 AND L3 AND L10

FILE 'CASREACT' ENTERED AT 09:27:03 ON 21 SEP 2006

L12 STRUCTURE UPLOADED
 L13 1 S L12 CSS
 L14 100 S L12 CSS FUL
 L15 13946 S ALKALI?
 L16 22 S L15 AND L14

=> d l12

L12 HAS NO ANSWERS

L12 STR

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

Structure attributes must be viewed using STN Express query preparation.

=> d bib abs fcrd 1-22

L16 ANSWER 1 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 144:22720 CASREACT

TI Method for producing 3,5-di-tert-butyl-4-hydroxybenzoic acid from
 2,6-di-tert-butylphenol

IN Otsuka, Ryoichi

PA Kabushiki Kaisha Ueno Seiyaku Oyo Kenkyujo, Japan

SO Eur. Pat. Appl., 7 pp.

CODEN: EPXXDW

DT Patent

LA English

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----|--|------|----------|-----------------|----------|
| PI | EP 1600436 | A1 | 20051130 | EP 2005-11460 | 20050527 |
| R: | AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, PL, SK, BA, HR, IS, YU | | | | |

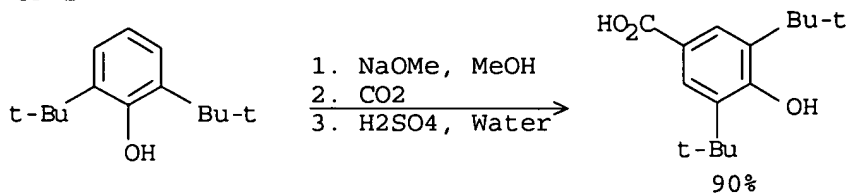
CAS ONLINE PRINTOUT

| | | | | |
|---------------|----|----------|------------------|----------|
| JP 2005336121 | A2 | 20051208 | JP 2004-158968 | 20040528 |
| CN 1704395 | A | 20051207 | CN 2005-10079277 | 20050527 |
| US 2005267311 | A1 | 20051201 | US 2005-139636 | 20050531 |
| US 7102028 | B2 | 20060905 | | |

PRAI JP 2004-158968 20040528

AB The present invention provides a method for producing 3,5-di-tert-butyl-4-hydroxybenzoic acid from 2,6-di-tert-butylphenol (DTBP), which may contain up to 0.5% by weight of 3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxybiphenyl (TTBBP), by reacting DTBP with a basic alkali metal compound, followed by reaction of the resulting alkali metal salt of DTBP with CO₂ to give the title compound in high and stable yield. For example, 1207 g of DTBP (containing 0.01% by weight of TTBBP) was reacted with 86.8 g of 28% solution of NaOMe in MeOH in a 2 L stainless-steel vessel and heated to 180° under N₂ for 2 h during which MeOH was distilled off. Next, the slurry of the obtained Na salt of DTBP was heated to 200°, and N₂ was replaced with CO₂ at 6 kgf/cm²(G) pressure with stirring for 2 h. The reaction mixture was cooled to 90° and 1200 g of water was added, followed by separation of aqueous and organic phases at 85° and addition of 73% aqueous sulfuric acid to precipitate 3,5-di-tert-butyl-4-hydroxybenzoic acid at 90.2% yield.

RX(2) OF 2



NOTE: thermal

CON: STAGE(1) 2 hours, 180 deg C
STAGE(2) 2 hours, 200 deg C, 6 kg/cm²
STAGE(3) pH 3.8

RE.CNT 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 2 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 143:117108 CASREACT

TI Phenol carboxylation with alkali metal salts of ethyl carbonic acid

AU Suerbaev, Kh. A.; Mikhnenko, O. E.; Akhmetova, G. B.; Shalmagambetov, K. M.; Chepaikin, E. G.

CS Kaz. Nats. Univ. im. Al-Farabi, Almaty, Kazakhstan

SO Neftekhimiya (2005), 45(1), 46-49

CODEN: NEFTAH; ISSN: 0028-2421

PB Nauka

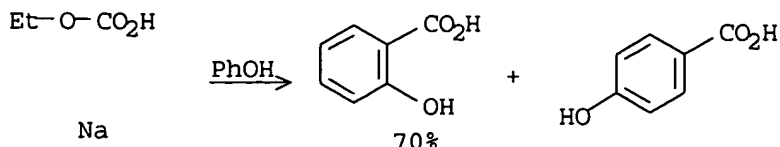
DT Journal

LA Russian

AB Phenol carboxylation with sodium ethylcarbonate under optimized reaction conditions comprising argon pressure of 1 MPa, temperature 200°, reaction time 6 h, yields 69.9% o-hydroxybenzoic and 17.5% p-hydroxybenzoic acid. A simple and convenient method of p-hydroxybenzoic acid is reported comprising phenol carboxylation with potassium ethylcarbonate.

CAS ONLINE PRINTOUT

RX(1) OF 2



NOTE: chemoselective, 88% overall yield, CO₂ or Ar used, Kolbe-Schmitt, alternative preparation shown, anaerobic, no solvent, optimization study, optimized on temperature, pressure, yield and mixture depends on temp.

CON: STAGE(1) 1 hour, 60 deg C, 1 MPa; 1 hour, 200 deg C

L16 ANSWER 3 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 141:243187 CASREACT

TI Process for production of hydroxybenzoic acids

IN Ueno, Ryuzo; Kitayama, Masaya; Otsuka, Ryoichi; Shirai, Takeshi

PA Kabushiki Kaisha Ueno Seiyaku Oyo Kenkyujo, Japan

SO PCT Int. Appl., 17 pp.

CODEN: PIXXD2

DT Patent

LA Japanese

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----|---------------|--|----------|------------------|----------|
| PI | WO 2004078693 | A1 | 20040916 | WO 2004-JP2554 | 20040302 |
| | W: | AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI | | | |
| | RW: | BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | |
| | EP 1600435 | A1 | 20051130 | EP 2004-716335 | 20040302 |
| | R: | AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, PL, SK | | | |
| | CN 1784373 | A | 20060607 | CN 2004-80011830 | 20040302 |
| | US 2006183939 | A1 | 20060817 | US 2005-547763 | 20050902 |

PRAI JP 2003-57260 20030304

WO 2004-JP2554 20040302

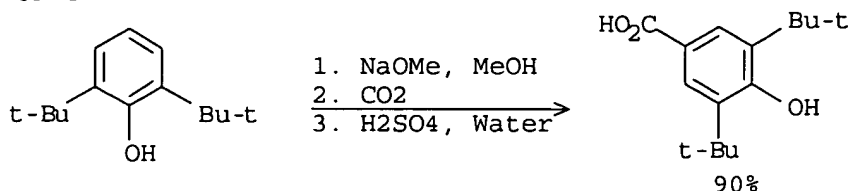
OS MARPAT 141:243187

AB Disclosed is a process for the production of hydroxybenzoic acids by Kolbe-Schmitt reaction which comprises the step of preparing an alkali metal phenolate from a phenol and the step of reacting the alkali metal phenolate with carbon dioxide, wherein the step of preparing an alkali metal phenolate comprises the following substeps (a) and (b): (a) the substep of reacting an alkali metal alkoxide with an excess of a phenol to form an alkali metal phenolate, and (b) the substep of removing an alc. formed in the step (a). According to the process, high-purity hydroxybenzoic acids can be inexpensively produced in high yield without using an aprotic polar organic solvent. Thus, 1,155 g 2,6-di(tert-butyl)phenol and 154 g 28% NaOMe/MeOH were added to a 2 L stainless steel reactor, heated to 180° under the stream of N, and allowed to react at the same temperature for 5 h while simultaneously distilling away MeOH formed to give a slurry of 2,6-di(tert-butyl)phenol sodium salt which was heated to 210°, purged with CO₂, and stirred under CO₂ pressure of 6 kgf/cm²(G) for 2 h, cooled to 90°, and treated with 1,200 g H₂O. The aqueous layer was

CAS ONLINE PRINTOUT

separated from the organic layer, adjusted to pH 3.8 by adding 73% aqueous H₂SO₄ and crystals precipitated was filtered, and dried to give 176 g 3,5-di(tert-butyl)-4-hydroxybenzoic acid (90% yield based on NaOMe).

RX(1) OF 4



NOTE: salt formation; Kolbe-Schmitt reaction; acidification

CON: STAGE(1) 5 hours, 180 deg C
 STAGE(2) 2 hours, 210 deg C, 5.8 atm
 STAGE(3) 90 deg C -> 85 deg C

RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 4 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 140:339070 CASREACT

TI Process for preparation of hydroxybenzoic acids

IN Ueno, Ryuzo; Kitayama, Masaya; Wakamori, Hiroyuki; Yonetani, Nobuhiro;
 Hisano, Takaya

PA Kabushiki Kaisha Ueno Seiyaku Oyo Kenkyujo, Japan

SO PCT Int. Appl., 12 pp.

CODEN: PIXXD2

DT Patent

LA Japanese

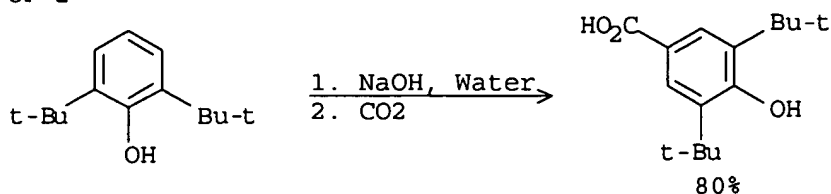
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---|------|----------|-----------------|----------|
| PI | WO 2004031113 | A1 | 20040415 | WO 2003-JP12458 | 20030930 |
| | W: CN, KR, US | | | | |
| | RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR | | | | |
| | JP 2004123592 | A2 | 20040422 | JP 2002-288732 | 20021001 |
| | EP 1559705 | A1 | 20050803 | EP 2003-799169 | 20030930 |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, SK | | | | |
| | CN 1684935 | A | 20051019 | CN 2003-823533 | 20030930 |
| | US 2006052632 | A1 | 20060309 | US 2005-529899 | 20050401 |
| PRAI | JP 2002-288732 | | 20021001 | | |
| | WO 2003-JP12458 | | 20030930 | | |

OS MARPAT 140:339070

AB This invention pertains to a method for producing hydroxybenzoic acids, which comprises reacting a phenol with an alkali metal compound through dehydration to form an alkali metal salt of the phenol and reacting the alkali metal salt with carbon dioxide at a temperature of 160 °C or above. For example, 2,6-di-tert-butylphenol was treated with aqueous NaOH and CO₂ at 210 °C with a pressure of 6 kgf/cm² to give 3,5-di-tert-butyl-4-hydroxybenzoic acid (80%). According to the process, hydroxybenzoic acids can be produced without using an aprotic polar organic solvent through easy means at a low cost. Further, the formation of byproducts is suppressed, so that high-purity hydroxybenzoic acids can be produced in high yield.

RX(1) OF 2



CON: STAGE(1) room temperature -> 210 deg C; 4 hours, 210 deg C
 STAGE(2) 2 hours, 210 deg C, 6 kPa

RE.CNT 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 5 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 137:216765 CASREACT

TI Recovery method of alkali metal salts in preparation of aromatic hydroxycarboxylic acids

IN Ueno, Ryuzo; Kitayama, Masaya; Izumichi, Nobutaka; Otsuka, Ryoichi; Yonetani, Nobuhiro

PA Ueno Fine Chemicals Industry Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 6 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

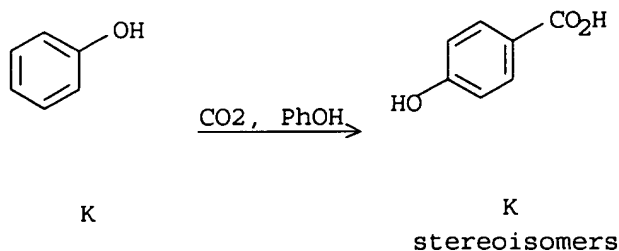
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---------------|------|----------|-----------------|----------|
| PI | JP 2002255891 | A2 | 20020911 | JP 2001-51984 | 20010227 |
| PRAI | JP 2001-51984 | | 20010227 | | |

AB Alkali metal salts are recovered by treating of aromatic hydroxycarboxylic acid alkali metal salts with mineral acids, addition of H2O-soluble organic solvents in the resulting solns. or slurries, crystallization of mineral acid alkali metal salts, and removal of the crystals from the aqueous solution A mixture of 414 g phenol potassium salt and

196 g phenol was treated with CO2 in gas oil to give 212 g p-hydroxybenzoic acid monopotassium salt and 237 g p-hydroxybenzoic acid dipotassium salt, which was mixed with water, extracted with xylene, treated with H2SO4, and crystallized to give 256 g K2SO4.

RX(1) OF 2



NOTE: thermal, high pressure

L16 ANSWER 6 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 137:109112 CASREACT

TI Effects of alkali and alkaline earth metals on the Kolbe-Schmitt reaction

AU Rahim, Mohammad Abdur; Matsui, Yoshihisa; Kosugi, Yoshio

CS Department of Life Science and Biotechnology, Faculty of Life and Environmental Sciences, Shimane University, Matsue, 690-8504, Japan

SO Bulletin of the Chemical Society of Japan (2002), 75(3), 619-622

CODEN: BCSJA8; ISSN: 0009-2673

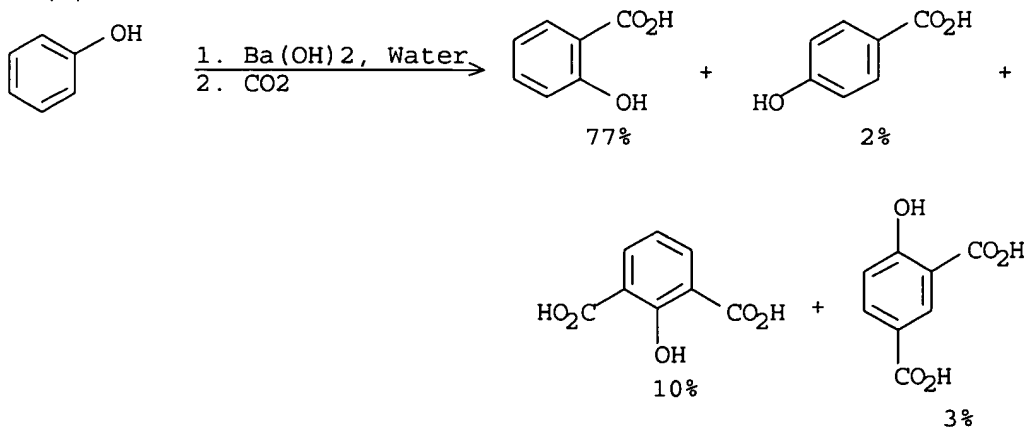
PB Chemical Society of Japan

DT Journal

LA English

AB It was found that the carboxylations of magnesium, calcium, and barium phenoxides with carbon dioxide at 260°C produced salicylic acid and dicarboxylic acids (4-hydroxyisophthalic acid and 2-hydroxyisophthalic acid) in very high yields (80-100%), exceeding that of the ordinary Kolbe-Schmitt reaction. The orientation (ortho/para ratio) was controlled not only by chelations of the intermediate with alkaline earth metal (Mg, Ca, Ba) ions, resulting in salicylic acid, but also by the sizes of metal ions (Rb, Cs), giving p-hydroxybenzoic acid in a much higher ratio than the widely used method with potassium or sodium phenoxide. These alkaline earth metals worked to produce 3-hydroxy-2-naphthoic acid by the reaction of 2-naphthoxide with carbon dioxide, but the yield of 6-hydroxy-2-naphthoic acid was comparable to that of 3-hydroxy-2-naphthoic acid when cesium or rubidium 2-naphthoxide was employed. Considerably high yields (.apprx.60%) of 6-hydroxy-2-naphthoic acid, a monomer of one of the best liquid-crystal polymers, was attained by the carboxylation of cesium or rubidium 2-naphthoxide in the presence of potassium or sodium carbonate, where the alkali metal ion was supposed to increase the reactivity of the substrate. The formation of "binol" was observed in the preparation of 2-naphthoxides with metal hydroxides, especially with copper(II) ion.

RX(1) OF 2



NOTE: Kolbe-Schmitt reaction, high pressure, thermal, no solvent, regioselective, optimization study of alkali and alk. earth metals

RE.CNT 19 THERE ARE 19 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 7 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

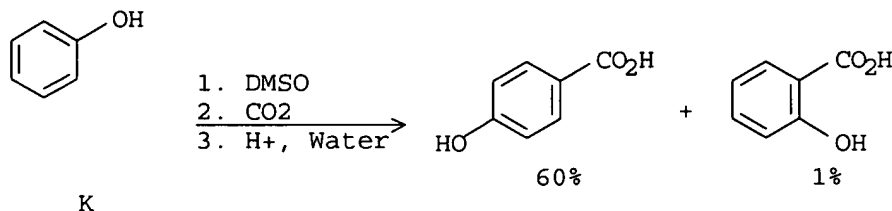
CAS ONLINE PRINTOUT

AN 134:222519 CASREACT
TI Method for producing hydroxyaromatic carboxylates that are rich in 4-hydroxybenzoate from carbon dioxide and alkali metal phenolates
IN Dinjus, Eckhard; Kunert, Michael; Wiegeleben, Peter
PA Forschungszentrum Karlsruhe G.m.b.H., Germany
SO PCT Int. Appl., 15 pp.
CODEN: PIXXD2
DT Patent
LA German
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|----|--|------|----------|-----------------|----------|
| PI | WO 2001017938 | A1 | 20010315 | WO 2000-EP8478 | 20000831 |
| | W: JP, US | | | | |
| | RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |

PRAI DE 1999-19942231 19990903
OS MARPAT 134:222519
AB Hydroxyarom. carboxylic acids (e.g., 4-hydroxybenzoic acid) are produced by reacting carbon dioxide with an alkali metal phenolate salt (e.g., sodium phenolate) with a dipolar aprotic liquid, (e.g., DMF). The sought after acid is formed as a main product together with comparatively low quantities of byproducts (e.g., salicylic acid).

RX(1) OF 1



NOTE: regioselective; autoclave (100.degree. end temp.); product ratios vary with temp.

RE.CNT 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

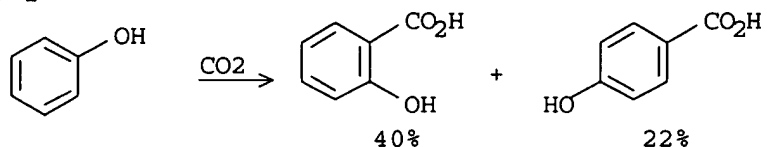
L16 ANSWER 8 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
AN 132:180370 CASREACT
TI Preparation of aromatic hydroxycarboxylic acids in a solvent-free system
IN Kosugi, Yoshio; Ueno, Ryuzo; Kitayama, Masanari
PA Ueno Seiyaku K. K., Japan
SO Jpn. Kokai Tokkyo Koho, 5 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|----------------|------|----------|-----------------|----------|
| PI | JP 2000072709 | A2 | 20000307 | JP 1998-244950 | 19980831 |
| PRAI | JP 1998-244950 | | 19980831 | | |

AB Aromatic hydroxycarboxylic acids are prepared by treatment of aromatic hydroxy compound alkali metal salts with CO₂ at ≤100° and ≥1 MPa (excluding CO₂ supercrit. condition) in a solvent-free

system. After the carboxylation reaction, CO₂ in the reaction system is replaced by inert gas, the reaction mixture is heated at 100-200°, then the carboxylation reaction is repeated. PhOK was autoclaved at 30° and 7.1 MPa CO₂ for 10 min, returned to normal pressure, purged with N, heated at 150° and 0.5 MPa N for 30 min, and treated with CO₂ at 7.1 MPa for 10 min to give 39.8% salicylic acid and 22.4% p-hydroxybenzoic acid.

RX(1) OF 1



NOTE: HIGH PRESSURE; TREATED TWICE WITH CO₂; REACTANT ALSO IN K SALT FORM

L16 ANSWER 9 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 131:44649 CASREACT

TI Preparation of aromatic hydroxy carboxylic acids

IN Kosugi, Yoshio; Ueno, Ryo; Kitayama, Masaya

PA Ueno Seiyaku K. K., Japan

SO Jpn. Kokai Tokkyo Koho, 5 pp.

CODEN: JKXXAF

DT Patent

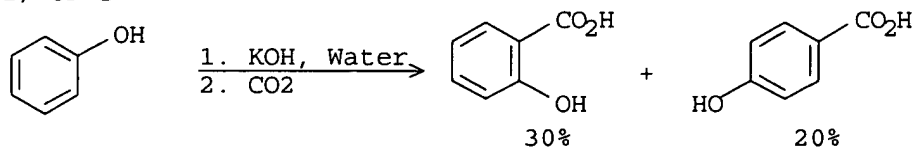
LA Japanese

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|----------------|------|----------|-----------------|----------|
| PI | JP 11171819 | A2 | 19990629 | JP 1998-244952 | 19980831 |
| PRAI | JP 1997-271153 | | 19971003 | | |

AB Title compds. were prepared by reaction of alkali metal salts of aromatic hydroxy compds. with CO₂ in the absence of solvent at >1 MPa, <100°, and under non-supercrit. condition. Thus, reaction of potassium salt of phenol with CO₂ at 5.0 MPa and 30° for 3 h gave 30.9% salicylic acid and 20.9% p-hydroxybenzoic acid.

RX(1) OF 1



L16 ANSWER 10 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 128:257241 CASREACT

TI Preparation of 3,5-dialkylsalicylic acids

IN Furuya, Masayuki; Nagatomo, Akinori; Wada, Masaru

PA Mitsui Toatsu Chemicals, Inc., Japan

SO Jpn. Kokai Tokkyo Koho, 5 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

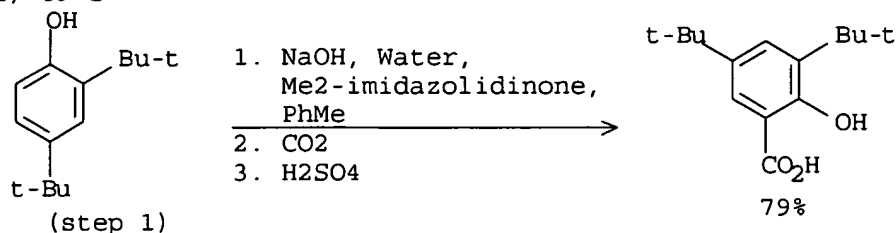
| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------------|------|------|-----------------|------|
|--|------------|------|------|-----------------|------|

PI JP 10087562 A2 19980407 JP 1996-242046 19960912

PRAI JP 1996-242046 19960912

AB Title compds., useful as materials for agrochems., antioxidants, developers for pressure-sensitive papers, are prepared by reaction of 2,4-dialkylphenols with alkali metal compds. and reaction of 2,4-dialkylphenol alkali metal salts with CO₂ in 1,3-dimethyl-2-imidazolidinone (I) as a reaction solvent in solution or slurry states. 2,4-Di-tert-butylphenol was dehydrated with NaOH in I-PhMe mixture in the presence of H₂O, carboxylated under heating and 6 kg/cm² CO₂ at 120° for 5 h, reacted with H₂SO₄ for 2 h to give 79.9% 3,5-di-tert-butylsalicylic acid.

RX(1) OF 1



L16 ANSWER 11 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 128:257240 CASREACT

TI Preparation of p-hydroxybenzoic acid from phenol alkali metal salts and carbon dioxide

IN Endo, Itaru; Imamura, Shinzo

PA Toray Industries, Inc., Japan

SO Jpn. Kokai Tokkyo Koho, 5 pp.

CODEN: JKXXAF

DT Patent

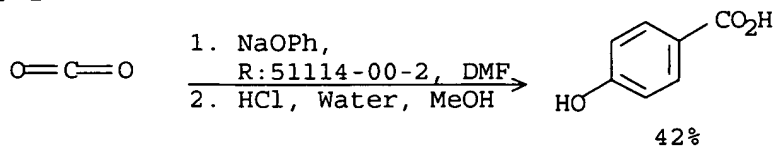
LA Japanese

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|-------------------|------|----------|-----------------|----------|
| PI | JP 10087558 | A2 | 19980407 | JP 1996-239492 | 19960910 |
| PRAI | JP 1996-239492 | | 19960910 | | |
| OS | MARPAT 128:257240 | | | | |

AB 4-HOC₆H₄CO₂H is prepared by treatment of alkali metal salts with CO₂ in aprotic polar solvents in the presence of alkali metal salts of compds. whose acidity is lower than that of PhOH. PhONa was treated at 95° for 16 h in DMF under CO₂ in the presence of 2,4,6-trimethylphenol Na salt to give 42.6% 4-HOC₆H₄CO₂H.

RX(1) OF 1



L16 ANSWER 12 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 128:257236 CASREACT

TI Preparation of hydroxybenzoic acids

CAS ONLINE PRINTOUT

IN Furuya, Masayuki; Nagatomo, Akinori; Wada, Masaru

PA Mitsui Toatsu Chemicals, Inc., Japan

SO Eur. Pat. Appl., 12 pp.

CODEN: EPXXDW

DT Patent

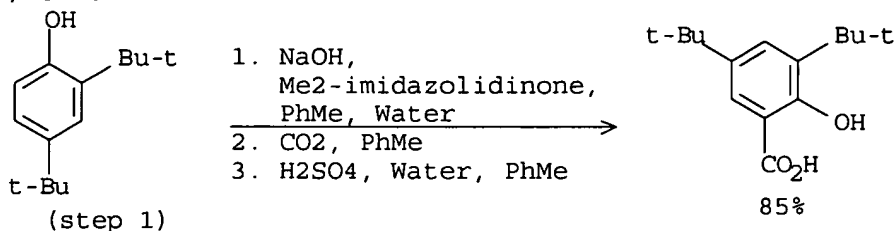
LA English

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---|------|----------|------------------|----------|
| PI | EP 834494 | A1 | 19980408 | EP 1997-307712 | 19970930 |
| | EP 834494 | B1 | 20010912 | | |
| | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO | | | | |
| | JP 10231271 | A2 | 19980902 | JP 1997-258483 | 19970924 |
| | JP 3739543 | B2 | 20060125 | | |
| | US 6392090 | B1 | 20020521 | US 1997-938833 | 19970926 |
| | TW 389752 | B | 20000511 | TW 1997-86114495 | 19971001 |
| PRAI | JP 1996-261715 | | 19961002 | | |
| | JP 1996-335516 | | 19961216 | | |

AB The title process comprises reacting a phenol in stoichiometric excess with an alkali metal compound in an aprotic polar organic solvent to form an alkali metal salt of the phenol and reacting this alkali metal salt with CO₂.

RX(1) OF 4



NOTE: high pressure second stage, extensive variations on work-up

RE.CNT 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 13 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 128:257231 CASREACT

TI Preparation of alkali metal phenoxide-aprotic polar solvent (1:2 mol) complexes and p-hydroxybenzoic acid

IN Endo, Itaru; Imamura, Shinzo

PA Toray Industries, Inc., Japan

SO Jpn. Kokai Tokkyo Koho, 5 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

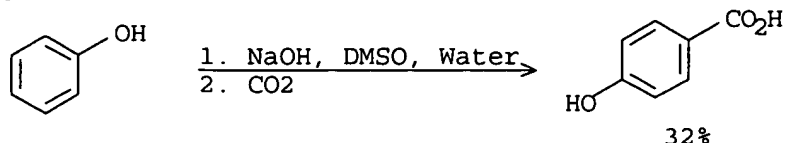
| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|----------------|------|----------|-----------------|----------|
| PI | JP 10087560 | A2 | 19980407 | JP 1996-239491 | 19960910 |
| PRAI | JP 1996-239491 | | 19960910 | | |

AB The title complexes, useful as intermediates for p-hydroxybenzoic acid (I), are prepared by treatment of PhOH with alkali metal hydroxides in aprotic polar solvents, followed by removal of H₂O. I is prepared by treatment of PhOH with alkali metal hydroxides in aprotic polar solvents, removing H₂O, and treatment with CO₂. PhOH (83.06 g) was treated with 70.07 g 19N aqueous NaOH in 326 g DMSO, then concentrated in

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vacuo to give 232.50 g PhONa-DMSO (1:2 mol) complex.

RX(1) OF 1



L16 ANSWER 14 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
 AN 128:167257 CASREACT
 TI Preparation of dialkyl hydroxybenzoic acids by carboxylation
 IN Tsuru, Kazutaka; Nagai, Naoshi; Ishitoku, Takeshi
 PA Mitsui Petrochemical Industries, Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 5 pp.
 CODEN: JKXXAF

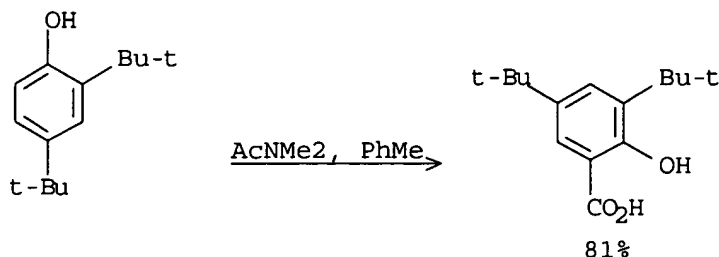
DT Patent
 LA Japanese

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|-------------------|------|----------|-----------------|----------|
| PI | JP 10059897 | A2 | 19980303 | JP 1997-101706 | 19970418 |
| PRAI | JP 1996-100021 | | 19960422 | | |
| OS | MARPAT 128:167257 | | | | |

AB Dialkyl hydroxybenzoic acids (I) was prepared by reacting alkali metal salt of dialkylphenol with CO₂ in the presence of amide R₁CONR₂R₃ (R₁ = H, C1-4 alkyl or alkoxy, etc.; R₂, R₃ = H, C1-4 alkyl, etc.; R₁ may combine with R₃ to form alkylene, etc.) in hydrocarbon solvents. I, useful as intermediates in the production of antioxidants, drugs and pesticides, are prepared in an industrial manner efficiently and economically. Thus, 2,4-di-tert-butylphenol sodium salt was reacted with CO₂ in the presence of MeCONMe₂ at 140° for 2.5 h under 0.50 MPa pressure to give 81.0% 3,5-di-tert-butylsalicylic acid.

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Na

NOTE: 140.degree. for 2.5 h under 0.50 MPa pressure

L16 ANSWER 15 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
 AN 116:235255 CASREACT
 TI process for controlling the isomer ratio of aromatic hydrocarboxylic acids in the carboxylation of alkali phenolates in phosphine oxide solvents

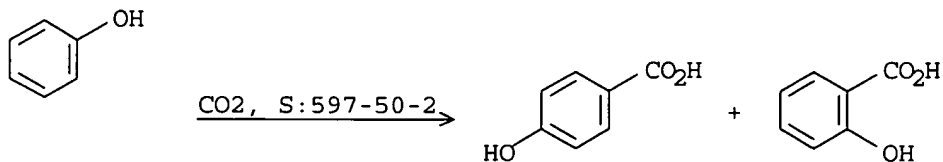
CAS ONLINE PRINTOUT

IN Nakanishi, Takehisa; Miura, Toshizumi
PA Mitsui Toatsu Chemicals, Inc., Japan
SO Eur. Pat. Appl., 13 pp.
CODEN: EPXXDW
DT Patent
LA English
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|-------------------|----------|----------|-----------------|----------|
| PI | EP 478197 | A1 | 19920401 | EP 1991-308418 | 19910916 |
| | R: DE, FR, GB | | | | |
| | JP 05009155 | A2 | 19930119 | JP 1991-213281 | 19910826 |
| PRAI | JP 1990-244099 | 19900917 | | | |
| OS | MARPAT 116:235255 | | | | |

AB A process for controlling the isomer ratio of aromatic hydrocarboxylic acids in the reaction of an alkali phenolate with CO₂ in an organic phosphine oxide solvent comprises the use of said phosphine oxide solvent and phenolate in varying ratios in the range from 1 to 4. A reactor was charged with Na phenolate (11.6 g) and tri-Et phosphine oxide (53.7 g) and carbon dioxide was blown through the mixture at 50° (adsorption) and then the internal temperature was raised to 140° and carbon dioxide was supplied for an addnl. 10 min. Conversion of Na phenolate was 30%; selectivity toward formation of 4-hydroxybenzoic acid (I) was 90% and selectivity toward formation of salicylic acid (II) was 9%. Traces of hydroxyisophthalic acid were formed. Carboxylation of sodium o-cresolate, sodium m-cresolate, or potassium o-phenylphenolate also gave I and II. Carboxylation of sodium 1-naphtholate gave 1-hydroxy-4-naphthalenecarboxylic acid and 1-hydroxy-2-naphthalenecarboxylic acid.

RX(1) OF 4



Na

NOTE: regioselective

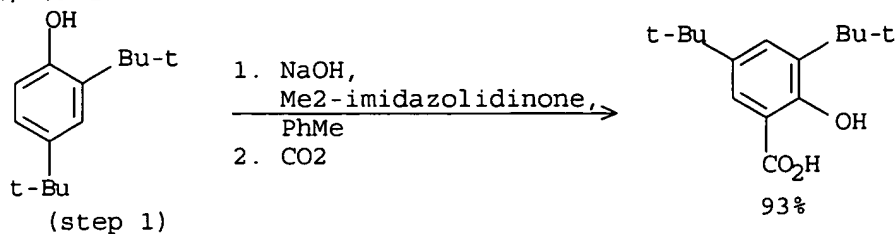
L16 ANSWER 16 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
AN 115:135686 CASREACT
TI Preparation of 3,5-dialkylsalicylic acids
IN Ike, Tetsuji; Kinishi, Ryoichi
PA Yoshitomi Pharmaceutical Industries, Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 3 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|--|----------|----------|-----------------|----------|
| PI | JP 03090047 | A2 | 19910416 | JP 1989-228091 | 19890901 |
| PRAI | JP 1989-228091 | 19890901 | | | |
| AB | The title compds., useful as materials for agrochems., antioxidants, developers for pressure-sensitive papers, etc., are prepared by heating | | | | |

CAS ONLINE PRINTOUT

2,4-dialkylphenols with alkali metal hydroxides in mixed solvents of hydrocarbons and 1,3-dimethyl-2-imidazolidinone (I) under azeotropic removal of H₂O and treating the resulting essentially anhydrous alkali metal salts with CO₂ in the above mixed solvents. A mixture containing 2,4-di-tert-butylphenol, toluene, I, and NaOH was heated under stirring, and H₂O was removed azeotropically. The residue was treated at 110-150° under 5 kg/cm² CO₂ for 4 h to give 98% (93% after purification) 3,5-di-tert-butylsalicylic acid, vs. 54% for a control without I.

RX(1) OF 1



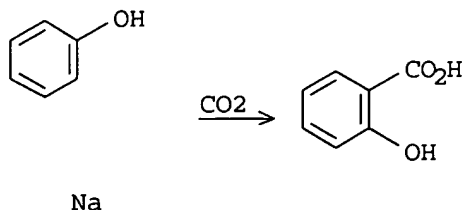
L16 ANSWER 17 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
 AN 113:190923 CASREACT
 TI Preparation of p-hydroxybenzoic acid
 IN Nakanishi, Takehisa; Hashimoto, Masao; Miura, Toshizumi
 PA Mitsui Toatsu Chemicals, Inc., Japan
 SO Eur. Pat. Appl., 8 pp.
 CODEN: EPXXDW
 DT Patent
 LA English
 FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|-------------------------------|------|----------|-----------------|----------|
| PI | EP 371721 | A2 | 19900606 | EP 1989-312271 | 19891127 |
| | EP 371721 | A3 | 19911106 | | |
| | EP 371721 | B1 | 19940727 | | |
| | R: CH, DE, FR, GB, IT, LI, NL | | | | |
| | JP 02223540 | A2 | 19900905 | JP 1989-287594 | 19891106 |
| | US 4950781 | A | 19900821 | US 1989-439701 | 19891121 |
| | CA 2004004 | AA | 19900529 | CA 1989-2004004 | 19891128 |
| PRAI | JP 1988-299627 | | 19881129 | | |

OS MARPAT 113:190923

AB Alkali metal salts of phenol are carboxylated to mixts. comprising high proportions of 4-HOC₆H₄CO₂H (I) in the presence of R₁R₂R₃PO (R₁-R₃ = C₁-8 alkyl, Ph) as solvents. Thus, CO₂ was blown for 1 h through a solution of PhOK in Me₃PO maintained at 140° to give 49.2% conversion with 97.1% selectivity for I.

RX(1) OF 2



CAS ONLINE PRINTOUT

L16 ANSWER 18 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
AN 111:114859 CASREACT

TI A process for the preparation of hydroxybenzoic acid
IN Sakai, Tsunenori; Ishiguro, Toshio; Ishihara, Takaya
PA Idemitsu Petrochemical Co., Ltd., Japan
SO Eur. Pat. Appl., 7 pp.

CODEN: EPXXDW

DT Patent

LA English

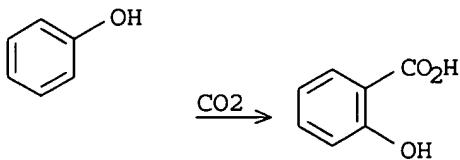
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---------------------------------------|------|----------|-----------------|----------|
| PI | EP 298289 | A2 | 19890111 | EP 1988-109719 | 19880617 |
| | EP 298289 | A3 | 19900711 | | |
| | EP 298289 | B1 | 19930512 | | |
| | R: BE, CH, DE, FR, GB, IT, LI, NL, SE | | | | |
| | JP 64003149 | A2 | 19890106 | JP 1987-157140 | 19870624 |
| | JP 64003150 | A2 | 19890106 | JP 1987-159097 | 19870626 |
| | JP 01113338 | A2 | 19890502 | JP 1987-269315 | 19871027 |
| | US 4814495 | A | 19890321 | US 1988-203345 | 19880606 |
| PRAI | JP 1987-157140 | | 19870624 | | |
| | JP 1987-159097 | | 19870626 | | |
| | JP 1987-269315 | | 19871027 | | |

AB The title compound, more specifically 4-HOC₆H₄CO₂H (I) is prepared by reaction of an alkali metal phenolate (obtained by reaction of PhOH and an alkali metal hydroxide) with CO₂, the product dissolved in H₂O, and the aqueous solution acidified with an inorg. acid to precipitate the title

compound which is separated from the mother liquor. The process comprises subjecting the acidified mother liquor to dehydration treatment followed by calcination, salting-out by blowing HCl(g) into the mother liquor and reverse osmosis to sep. the alkali metal salt contained in the mother liquor, and subjecting the alkali metal salt to electrolysis to form an alkali metal hydroxide, and recovering the alkali metal hydroxide. PhOK and CO₂ (pressure 5 kg/cm²) were heated to 230° for 10 min, cooled to 80°, H₂O was added, and the aqueous solution acidified to give a precipitate containing I.

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K

L16 ANSWER 19 OF 22 CASREACT COPYRIGHT 2006 ACS on STN

AN 107:115368 CASREACT

TI 3,5-Di-tertiary-butylsalicylic acid

IN Takada, Sohei; Miyamoto, Kazuo

PA Daiei Kako K. K., Japan

SO Jpn. Kokai Tokkyo Koho, 3 pp.

CODEN: JKXXAF

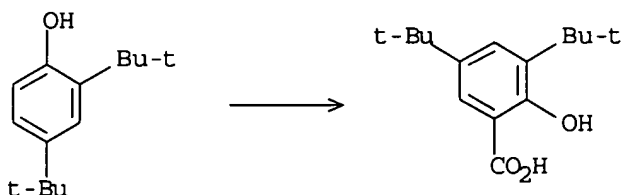
CAS ONLINE PRINTOUT

DT Patent
LA Japanese
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|----------------|------|----------|-----------------|----------|
| PI | JP 62061949 | A2 | 19870318 | JP 1985-201230 | 19850911 |
| PRAI | JP 1985-201230 | | 19850911 | | |

AB Title compound (I), useful as a charge controlling agent for PPC electrophotog. toners, was prepared by treating a mixture of 2,4-(Me₃C)₂C₆H₃OH (II) and alkali hydroxides with CO₂ without solvents. Thus, an aqueous solution of 56.0 g KOH was added to 20.6 g II and the mixture was dehydrated at 100° under 50 mmHg. The resulting product was ground and autoclaved at 140-160° under 9-13 kg/cm² CO₂ to give 93% I.

RX(1) OF 1



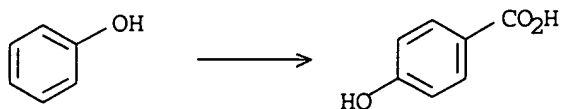
L16 ANSWER 20 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
AN 105:226054 CASREACT
TI Aromatic hydroxycarboxylic acid
IN Ueno, Ryuzo; Kanagae, Toshiharu; Kishimoto, Mitsuyuki
PA Kabushiki Kaisha Ueno Seiyaku Oyo Kenkyujo, Japan
SO PCT Int. Appl., 16 pp.
CODEN: PIXXD2

DT Patent
LA Japanese

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|-----------------------------------|------|----------|-----------------|----------|
| PI | WO 8602924 | A1 | 19860522 | WO 1985-JP626 | 19851109 |
| | W: KR, US | | | | |
| | RW: BE, CH, DE, FR, GB, IT, NL | | | | |
| | JP 61115053 | A2 | 19860602 | JP 1984-235033 | 19841109 |
| | EP 201607 | A1 | 19861120 | EP 1985-905672 | 19851109 |
| | EP 201607 | B1 | 19911030 | | |
| | R: BE, CH, DE, FR, GB, IT, LI, NL | | | | |
| | CA 1263868 | A1 | 19891212 | CA 1986-508469 | 19860506 |
| | US 4780567 | A | 19881025 | US 1986-887037 | 19860701 |
| PRAI | JP 1984-235033 | | 19841109 | | |
| | WO 1985-JP626 | | 19851109 | | |

AB The title acids are prepared by reaction of an aromatic hydroxy compound, its alkali salt, and a polycyclic aromatic hydrocarbon with CO₂ in the liquid phase. Thus, CO₂ was introduced into a mixture of PhOK 100, PhOH 35, and hydrogenated terphenyl 400 g at 250° and 7 kg/cm² gage to give 77.3% p-HOC₆H₄CO₂H of 100% purity with 99.7% selectivity.

RX(1) OF 1



CAS ONLINE PRINTOUT

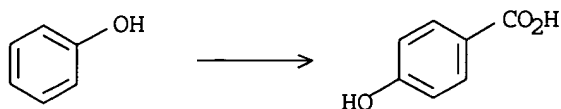
L16 ANSWER 21 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
AN 104:34089 CASREACT
TI p-Substituted phenol derivatives
IN Hirai, Hidefumi; Komiyama, Makoto; Sugiura, Izuru
PA Japan
SO PCT Int. Appl., 53 pp.
CODEN: PIXXD2
DT Patent
LA Japanese
FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|-------------------------------|------|----------|-----------------|----------|
| PI | WO 8503701 | A1 | 19850829 | WO 1985-JP57 | 19850213 |
| | W: AU, US | | | | |
| | RW: BE, CH, DE, FR, GB, NL | | | | |
| | JP 60169438 | A2 | 19850902 | JP 1984-25589 | 19840214 |
| | JP 60215645 | A2 | 19851029 | JP 1984-73300 | 19840412 |
| | JP 60222438 | A2 | 19851107 | JP 1984-79067 | 19840419 |
| | AU 8539385 | A1 | 19850910 | AU 1985-39385 | 19850213 |
| | AU 576457 | B2 | 19880825 | | |
| | EP 173748 | A1 | 19860312 | EP 1985-901054 | 19850213 |
| | EP 173748 | B1 | 19900103 | | |
| | R: BE, CH, DE, FR, GB, LI, NL | | | | |
| | CA 1234393 | A1 | 19880322 | CA 1985-478691 | 19850410 |
| | US 4663478 | A | 19870505 | US 1985-725360 | 19850418 |
| PRAI | JP 1984-25589 | | 19840214 | | |
| | JP 1984-73300 | | 19840412 | | |
| | JP 1984-79067 | | 19840419 | | |
| | WO 1985-JP57 | | 19850213 | | |

OS MARPAT 104:34089

AB The title derivs. were prepared by substitution of the phenol derivs. with organic halides such CHX3 (X = halo), CX4, or H2C:CHCH2X in the presence of alkali hydroxides over immobilized cyclodextrin catalysts crosslinked through the HO groups with a divalent hydrocarbon radical having free valences at both ends, optionally substituted by alkyl, halo, HO, O, S, or phenylene. Thus, 50 mg NaBH4 was added to a solution of 50 g β -cyclodextrin in 50% aqueous NaOH followed by epichlorohydrin under stirring and heating at 50° to give the immobilized catalyst, over which (1.5 g) was refluxed a mixture of 1.5 g PhOH, 3 mL CCl4, and 0.1 g Cu powder in 20% aqueous NaOH to give 91 mol% p-HOC6H4CO2H with 100% selectivity.

RX(1) OF 2



L16 ANSWER 22 OF 22 CASREACT COPYRIGHT 2006 ACS on STN
AN 94:17307 CASREACT
TI Oxidation of creosol with oxygen in alkaline solution. Model experiments on oxygen pulping of wood
AU Fricko, Paul; Holocher-Ertl, Martin; Kratzl, Karl
CS Inst. Org. Chem., Univ. Wien, Vienna, A-1090, Austria
SO Monatshefte fuer Chemie (1980), 111(5), 1025-41

CAS ONLINE PRINTOUT

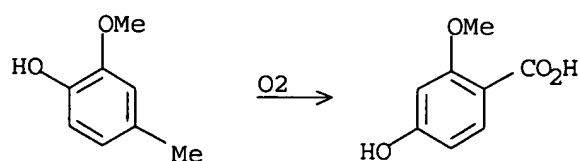
CODEN: MOCMB7; ISSN: 0026-9247

DT Journal

LA German

AB The degradation of 2-methoxy-4-methylphenol [93-51-6], 4-(hydroperoxy)-2-methoxy-4-methyl-2,5-cyclohexadienone [75770-63-7], 4-hydroxy-2-methoxy-4-methyl-2,5-cyclohexadienone [42860-79-7], 5,6-epoxy-4-hydroxy-2-methoxy-4-methyl-2-cyclohexenone [71843-96-4], 2-methoxy-1,4-benzoquinone [2880-58-2], and 3-methylmuconic acid [17110-47-3] as models for lignin [9005-53-2] with O or H₂O₂ in the presence of NaOH gave carboxylic acids and neutral substances. The degradation products of these model compds. were also identified by gas chromatog.-mass spectroscopy.

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